PERGAMON

Renewable and Sustainable Energy Reviews
5 (2001) 137–155

RENEWABLE
& SUSTAINABLE
ENERGY REVIEWS

www.elsevier.com/locate/rser

An appraisal of electric automobile power sources

A.K. Shukla [a], A.S. Aricò [b], V. Antonucci [b,*]

[a] *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*
[b] *Institute CNR-TAE, Via Salita S. Lucia sopra Contesse, n. 5, 98126 Messina, Italy*

Received 30 May 2000; received in revised form 10 July 2000; accepted 16 August 2000

Abstract

Road transportation, as an important requirement of modern society, is presently hindered by restrictions in emission legislations as well as the availability of petroleum fuels, and as a consequence, the fuel cost. For nearly 270 years, we burned our fossil cache and have come to within a generation of exhausting the liquid part of it. Besides, to reduce the greenhouse gases, and to obey the environmental laws of most countries, it would be necessary to replace a significant number of the petroleum-fueled internal-combustion-engine vehicles (ICEVs) with electric cars in the near future. In this article, we briefly describe the merits and demerits of various proposed electrochemical systems for electric cars, namely the storage batteries, fuel cells and electrochemical supercapacitors, and determine the power and energy requirements of a modern car. We conclude that a viable electric car could be operated with a 50 kW polymer-electrolyte fuel cell stack to provide power for cruising and climbing, coupled in parallel with a 30 kW supercapacitor and/or battery bank to deliver additional short-term burst-power during acceleration.

Keywords: Fuel cells; Batteries; Supercapacitors; Electric vehicles

Contents

1. Introduction 138

* Corresponding author. Tel.: +39-090-624234; fax: +39-090-624247.
E-mail address: antonucci@itae.me.cnr.it (V. Antonucci).

PII: S1364-0321(00)00011-3

2. Power and energy estimates for an electric car 139

3. Electrochemical energy conversion and storage systems 142
3.1. Storage batteries 142
3.1.1. Lead-acid batteries 142
3.1.2. Nickel-cadmium batteries 143
3.1.3. Nickel-metal hydride batteries 143
3.1.4. Zinc-air batteries 144
3.1.5. Lithium secondary batteries 144
3.1.6. High-temperature zebra batteries 145
3.2. Fuel cells 146
3.2.1. Phosphoric acid fuel cells (PAFCs) 146
3.2.2. Alkaline fuel cells (AFCs) 147
3.2.3. Molten carbonate fuel cells (MCFCs) 147
3.2.4. Solid oxide fuel cells (SOFCs) 147
3.2.5. Polymer-electrolyte fuel cells (PEFCs) 147
3.2.6. Solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs) 148
3.3. Electrochemical supercapacitors 148

4. Assessment of electrochemical power sources for electric cars 149

5. Conclusions 154

Appendix A 154
A.1. Estimation of P_{tyres} at vehicle speed (v) of 50 and 100 km/h 154
A.2. Estimation of P_{aero} at vehicle speed (v) of 50 and 100 km/h 155
A.3. Estimation of P_{grade} at 10% gradient and v =80 km/h 155
A.4. Estimation of P_{accel} at v =50 and 100 km/h with an acceleration of 5km/h/s . 155

References 155

1. Introduction

Deteriorating urban air-quality, growing dependence on insecure energy sources, and global warming are forcing the re-examination of petroleum-fueled ICEVs as the basis for road transportation throughout the world. Although modern cars emit far less toxic pollutants comprising hydrocarbons, nitrogen oxides, carbon-monooxide and particulates, their increasing number is resulting in growing insistence to reduce automobile pollution further and further. At present, motor vehicles account for about one-half of the total hydrocarbon and nitrogen oxide pollution which combine to form ground-level ozone, commonly known as smog, that chokes many of the major urban centers of the world. This has brought in emission legislation all over the world, particularly in the light of the Kyoto Protocol [1], requiring the introduction of zero-emission vehicles (ZEVs). This had been thought to mean battery-powered cars. But, the battery-powered cars are found to be doubtful starters

[2,3]. Furthermore, batteries need electricity, which would be generated by burning coal to CO_2 and SO_2. By contrast, the argument of fuel cells with on-board reforming of a fossil fuel to produce hydrogen is both politically and scientifically more convincing. The conversion of methanol to hydrogen for producing electricity in a fuel cell will help in reducing the production of CO_2 gas by about 33% and there will be virtually no other polluting gases.

In this article, we estimate the power and energy requirements of a modern car, and examine the feasibility of the various available electrochemical energy conversion and storage options for realizing a viable electric-drive-system.

2. Power and energy estimates for an electric car

In order to properly assess the use of the electrochemical energy conversion and storage systems, viz. the storage batteries, supercapacitors and fuel cells, to power electric vehicles, it is mandatory to quantitatively estimate the power and energy required for propelling a modern car. Neglecting relatively minor losses due to road camber and curvature, the power required at the drive wheel (P_{traction}) may be expressed as [4],

$$P_{\mathrm{traction}}=P_{\mathrm{grade}}+P_{\mathrm{accel}}+P_{\mathrm{tyres}}+P_{\mathrm{aero}}+P_{\mathrm{inertial}} \quad (1)$$

where P_{grade} is the power required for the gradient, P_{accel} is the power required for acceleration, P_{tyres} is the rolling resistance power consumed by the tyres, P_{aero} is the power consumed by the aerodynamic drag and P_{inertial} include inertial losses of rotating components.

The first two terms in Eq. (1) describe the rates of change of potential (PE) and kinetic (KE) energies associated during climbing and acceleration, respectively. The power required for these actions may be estimated from the Newtonian kinematics as follows.

$$P_{\mathrm{grade}}=d(PE)/dt=Mgv\sin\theta \quad (2)$$

and,

$$P_{\mathrm{accel}}=d(KE)/dt=d(1/2Mv^2)/dt=Mav \quad (3)$$

where M is the mass of the car, v is its velocity, a is its acceleration, and $\tan\theta$ is the gradient. The potential and kinetic energies required by the car as a result of climbing and acceleration represent reversibly stored energies and, in principle, may be recovered by appropriate regenerative methods wherein the mechanical energy is converted and stored as electrical energy.

The last two terms in Eq. (1) describe the power which is required to overcome tyre friction and aerodynamic drag that are irreversibly lost, mainly as heat and noise and cannot be recovered. The power required here may be estimated from the following empirical relations.

$$P_{\mathrm{tyres}}=C_{\mathrm{t}}Mgv \quad (4)$$

and,

$$P_{aero}=0.5dC_aA(v+w)^2v \quad (5)$$

where C_t and C_a are dimensionless tyre friction and aerodynamic drag coefficients, respectively, d is the air density, w is the head-wind velocity, g is the gravitational acceleration, and A is the frontal cross-sectional area of the car.

From the parameters associated with a typical modern medium-size car, viz. M=1400 kg, A=2.2m^2, C_t=0.01, C_a=0.3, d=1.17 kg/m^3, its power requirements may be estimated from Eqs. (2)–(5). For the irreversible losses, Eqs. (4) and (5) show that while P_{tyres} is linearly dependent on velocity, P_{aero} varies as the third power of velocity and although negligible at low velocities, the latter becomes the dominant irreversible loss at high speed. As an example, for these parameters, for a car travelling at about 50 km/h, tyre friction is twice the aerodynamic drag and together amount to about 3 kW. At 100 km/h highway cruising, aerodynamic drag increases considerably to over twice the tyre friction, increasing the total power requirement to about 12 kW. It is noteworthy that for both these estimates, the wind speed (w) has been taken to be zero for the sake of simplicity (see Appendix A). But, in practice, the effect of wind speed on the performance of the car could be quite substantial, as shown in Fig. 1. Taking the example of a hill with a substantial 10% gradient, climbing at 80 km/h requires about 38 kW, including tyre friction and aerodynamic drag (see Appendix A). Acceleration is more demanding, particularly at high velocities. For example, acceleration at 5 km/h/s requires 30 kW at 50 km/h and increases to 66 kW at 100 km/h (see Appendix A).

The above estimates are for the power supplied to the wheel of the car and do

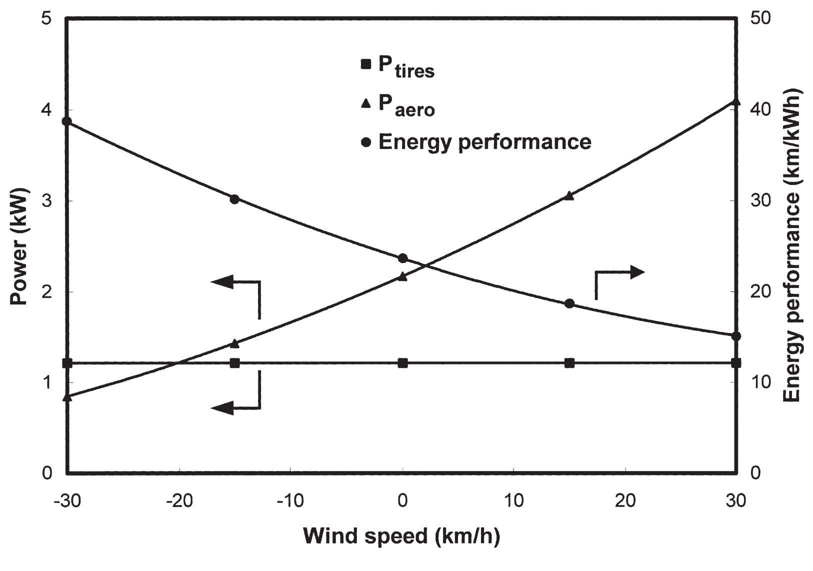


Fig. 1. Energy performance and power requirements of the car as a function of wind speed at vehicle speed of 80 km/h (after [4]).

not include the losses incurred in delivering that power to the wheels. At this time, in the development of electric-traction systems, a precise estimate of this is difficult to obtain but anecdotal information suggests that the efficiency of the power conditioning electronics together with the electrical and mechanical drive-train ($\varepsilon_{\mathrm{drive}}$) is likely to be about 0.85 on average. Additional power (P_{access}) may also be required to power the accessories like radio, lights, steering, and air-conditioning, etc., which is likely to add about 5 kW to the total power demand of the car.

In this way, the instantaneous total power required from the electric power-system (P_{total}) will be given by,

$$P_{\mathrm{total}}=P_{\mathrm{traction}}/\varepsilon_{\mathrm{drive}}+P_{\mathrm{access}} \tag{6}$$

An analysis of this kind indicates that the power plant of a modern car must be capable of delivering about 50 kW of sustained power for accessories and hill climbing, with peak-power requirement for a few tens of seconds to about 80 kW during acceleration. For a car with these performance characteristics, this sets the upper power limit required, but in common usage rarely exceeds 15 kW while cruising.

Eqs. (2)–(5) show that with the exception of aerodynamic losses, the power requirements scale with the mass of the car. While new light-weight materials and construction methods, together with design innovations to minimize aerodynamic drag may be able to reduce the power and energy requirements of the car, gains in excess of about 25% will be difficult to realize within an acceptable cost regime.

The energy consumed by a car is simply the time integral of the traction and accessory power plus that consumed by the power plant at idle (E_{idle}). Accordingly,

$$E_{\mathrm{total}}=\int P_{\mathrm{total}}dt+E_{\mathrm{idle}} \tag{7}$$

E_{total} depends on the nature of the drive cycle that the car is required to perform. Several estimates have been made for selection of acceleration–climb–cruise–idle sequences designed to simulate common driving practices. As with the power requirements of the car, E_{total} is very dependent on car mass. For the car parameters listed above, this may be expected to be near 200 Wh/km (Table 1).[1]

From this quantitative analysis of the power and energy requirements of a car, we will objectively evaluate the suitability of various electrochemical energy conversion and storage options in the following sections.

[1] Taking the heating value of gasoline as 32.49 MJ/l (see Table 1), a heating value of only 6.5 MJ/l will be achievable with an internal combustion engine of near 20% well-to-wheel efficiency. This is about 1.82 kWh/l of the gasoline and considering the average drive range of the car as about 10 km/l, it would amount to 182 Wh/km. The heating value for the diesel fuel is 35.95 MJ/l (see Table 1). Accordingly, the estimated E_{total} will be 201 Wh/l with the diesel-driven cars which have well-to-wheel efficiency of about 30% and a drive range of ~15 km/l.

Table 1
Properties of diesel fuel and gasoline

Physical properties	Diesel	Gasoline
Molecular wt. (-)	208	99
Density @ 20°C (kg/l)	0.84	0.74
Carbon content (% mass)	86.1	84.9
Oxygen (% mass)	0	0
Exhaust water (g/MJ)	28.6	30.3
Exhaust CO_2 (g/MJ)	74.2	73.3
Heat of evaporation (kJ/MJ)	5.9	8.5
Lower calorific value (MJ/kg)	42.8	43.9
Cetane number (-)	~50	~8

3. Electrochemical energy conversion and storage systems

The electrochemical systems, which have been envisaged as power sources for an electric car, comprise the storage batteries, fuel cells, and electrochemical supercapacitors. We will briefly introduce these systems in the following sub-sections.

3.1. Storage batteries

Storage batteries store a fixed amount of chemical energy and may be recharged when the electrochemically active materials in them have been exhausted. In the literature [5], several storage batteries have been proposed for electric cars. In the following sub-sections, we will briefly describe some of the promising storage batteries for electric cars.

3.1.1. Lead-acid batteries

The storage battery most commonly known to us is the lead-acid battery. The lead-acid battery is one of the most successful electrochemical systems ever developed. Although it was first demonstrated as early as in 1859 by Plantè and many other storage batteries have been developed since then, the lead-acid battery is still the most widely used storage battery. There are three types of lead-acid batteries in common use: (a) batteries with excess or flooded electrolyte, (b) low-maintenance batteries with a large excess of electrolyte, and (c) batteries with immobilized electrolyte and with a pressure-sensitive valve usually referred to as valve-regulated lead-acid (VRLA) or sealed lead-acid (SLA) batteries.

The conventional flooded-type lead-acid battery requires checking of specific gravity of electrolyte, periodic addition of water to maintain electrolyte above the plates and recharge soon after the battery discharge to prevent hard sulfation that causes loss of capacity. The emission of acid fumes causes corrosion of metallic parts in the vicinity of the battery. The seepage of acid on the top cover leads to leakage current resulting in increased self-discharge and ground-shunt hazards.

To overcome these problems VRLA or SLA batteries based on oxygen-recombi-

nation cycle have emerged. SLA batteries offer the freedom of battery placement, cyclability without the addition of water or checking the specific gravity, increased safety and superior performance in some instances.

The key issues which in the past have made the lead-acid batteries fail are short-life, high-maintenance, and inadequate energy density. Additional issues such as safety, environmental impact and material recyclability are becoming more critical than in the past. Keeping these factors in mind, manufacturers of storage batteries are exploring other technologies.

3.1.2. Nickel-cadmium batteries

At present, nickel-cadmium (Ni-Cd) batteries represent the best balance between specific energy, specific power, cycle-life and reliability. The Ni-Cd battery has a positive plate of nickel oxy-hydroxide (NiOOH), a negative plate of cadmium (Cd), and an aqueous solution of potassium hydroxide (KOH) for the electrolyte. The battery can endure a lot of abuse both physically and electrically. Also, the alkaline electrolyte does not enter into the discharge reaction as the acid does in the lead-acid battery and hence does not get depleted as the battery discharges. During discharge, NiOOH in the positive plate is converted to $Ni(OH)_2$. This reaction results in a change in the Ni-oxidation state from +3 to +2. During the cell recharge, NiOOH is retrieved. The cadmium of the negative plate is converted to $Cd(OH)_2$ during the cell discharge and retrieved during the cell charge.

Due to their high cranking-power, lower weight and corrosion-free atmosphere, nickel-cadmium batteries have found ample applications in defense and space. Nickel-cadmium batteries are produced mainly in (a) sintered plate, and (b) pocket-plate configurations. Recently, fiber nickel-cadmium batteries which employ fibers of foam nickel have been developed and commercialized.

Nickel-cadmium batteries, however, suffer from the memory effect, which burdens the user with having to at least occasionally follow a time-consuming recharging regime in order to maintain their rated capacity. The effect appears to be due to the growth of abnormally large crystals on cadmium electrode. These crystals reduce the surface area of the cadmium electrode, thereby increasing the battery’s effective internal resistance. Besides, nickel-cadmium batteries store only slightly more energy per unit weight than lead-acid units, have a fairly high-rate of self-discharge at high temperatures. Worst of all, cadmium is an awful poison that can contaminate the environment.

3.1.3. Nickel-metal hydride batteries

The unpopularity of cadmium has encouraged the development of nickel-metal hydride (Ni-MH) batteries, which are not only cadmium-free but can also store more energy than comparatively sized nickel-cadmium units. Similar to nickel-cadmium batteries, the Ni-MH units also employ nickel positive plates with NiOOH as the active material and an aqueous KOH electrolyte. The main difference is that the active material in the negative plate is hydrogen absorbed in a metal alloy. The metal alloys in which hydrogen is stored fall into two categories: (a) the AB_5-alloys based on mixtures of nickel and rare earth, and (b) the AB_2-alloys based on nickel com-

monly blended with titanium, vanadium, and zirconium. A typical composition of the AB_5-alloy that has been documented to be a promising electrode material is Mm (Mm = Misch metal: 25 wt.% La, 50 wt.% Ce, 7 wt.% Pr, 18 wt. Nd) $Ni_{3.2}$ $Co_{1.0}$ $Mn_{0.6}Al_{0.11}Mo_{0.09}$ which has $CaCu_5$-type crystal structure. Among the AB_2-type alloys, $Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}$ has been found to be an attractive electrode material, which has ^{14}C-Laves crystal structure. Although, in the beginning, AB_5-type alloys were employed as battery electrodes, but at present, AB_2-type alloys are preferred electrode materials for Ni-MH batteries. It is found that while AB_2-type alloys yield superior energy storage densities, the AB_5-alloys are able to hold hydrogen better thus lowering the self-discharge rate of the battery. It is noteworthy that the metal hydride electrode offers an important advantage for materials engineering and optimization in relation to negative electrodes of other nickel-based batteries.

On the down side, Ni-MH batteries deliver less power, have a faster self-discharge and are less tolerant to overcharge like the nickel-cadmium batteries; moreover, they are about five times more expensive than lead in automobile applications and are adversely impacted by warm temperature.

3.1.4. Zinc-air batteries

The very latest rechargeable zinc-air battery technology that uses a rechargeable air-electrode is claimed to move from the research laboratory to the market.

A zinc-air battery can store much larger energy in relation to a comparatively sized Ni-MH battery but zinc-air units require an air-management system to ensure the appropriate flow of air into the battery to generate the required power. Also, there is the need to remove carbon dioxide from air to avoid carbonation of the KOH electrolyte. Another weak point of these batteries is their sensitivity to electrical abuse. The batteries cannot be quick charged and if these are discharged below about 0.9 V/cell (operating cell-voltage ranges between 1–1.2 V), these batteries could be permanently damaged. Moreover, they have poor power density, so have to be complemented with a high power battery or ultracapacitor.

3.1.5. Lithium secondary batteries

The most promising system among the lithium secondary batteries is the lithium-ion battery, which is better known as lithium-ion rocking chair battery. In the unit, both the electrodes comprise intercalation materials with structure in which guest species are inserted and extracted with little structural modification of the host. The fully charged negative plate is made of lithiated carbon, which is about 10% lithium by weight and has nearly the same potential as metallic lithium. The discharged positive plate employs one of the intercalation compounds among $LiCoO_2$, $LiNiO_2$, $LiMnO_2$ or $LiMn_2O_4$, each of which develops a voltage between 3.5–4 V with respect to lithium.

Unlike conventional acidic and alkaline storage batteries, rocking-chair cells employ non-aqueous electrolytes comprising a lithium salt dissolved in an organic solvent. The main issues in selecting an electrolyte are its compatibility and thermal stability up to about 80°C. If the negative electrode consists of lithiated graphite, then the choice of the electrolyte is restricted to systems based on ethylene carbonate

since those based on other solvents tend to cause exfoliation of the graphite. The use of lithiated coke for the negative plate provides a much wider choice with diethyl carbonate, propylene carbonate, dimethyl carbonate, and many other solvents that may be used simply or in combination. The favorite solute is lithium hexafluorophosphate ($LiPF_6$) but other lithium salts may as well be used. The ionic conductivity of these mixtures is about two orders of magnitude lower than that of aqueous electrolytes but is high enough to make practical batteries for use at or above room temperatures. Actually, even at 0°C the ionic conductivity of 10^{-3} S cm^{-1} for these electrolytes suffices for the practical batteries. The conductivity, however, varies quite appreciably with temperature, and ranges from 0.2×10^{-3} at -40°C to 1.5×10^{-2} S cm^{-1} at 40°C for $LiPF_6$ dissolved in 1:1 volume mixture of ethylene carbonate and propylene carbonate. During the cell operation, lithium ions move back and forth between the two plates across the electrolyte as the unit is alternatively charged and discharged.

The lithium-ion cell is not the ultimate in the lithium secondary battery technology as far as the capacity is concerned. In principle, cells with negative electrodes of metallic lithium can store about ten-times more energy per unit weight than those with negative plates of lithiated carbon. The trouble is that the lithium electrode has a tendency to react with any liquid electrolyte creating a passive film. The reaction would have little effect if it happened only once but every time lithium is stripped away and then recharged, a fresh metal surface is exposed to the electrolyte and new film is formed. This process would use-up a lot of lithium. Partially because of these difficulties, research is being focussed on lithium batteries with solid-polymer electrolytes, which would be backed by highly conducting current-collector. These cells will be less than a half mm in thickness. A layered structure of this type, if realized, would have many attractions. Batteries of such cells could be made in almost any desired shape and size. The lack of liquid would make them fairly safe; these would have the highest specific energy rating among any known battery, and would also hold their charge for years with little loss. On the other hand, in automotive applications these batteries require a sophisticated voltage management system to prolong their life and prevent thermal runaway.

3.1.6. High-temperature zebra batteries

Over the years, significant modifications have also been made in the high-temperature sodium-sulfur (Na-S) batteries. The problem of dendritic-sodium growth in Na-S batteries has been cleverly circumvented in the zebra[2] batteries with the use of $NaAlCl_4$ in conjunction with Na^+-β-alumina ceramic electrolyte.

Since the zebra batteries operate at ~300°C, there are no detrimental effects resulting from their use at extremely cold or hot ambient-temperatures. For conventional battery systems, extreme temperatures require more elaborate thermal management or result in reduced battery performance. Besides, because of their high-tem-

[2] This battery was invented in 1985 by Coetzer in Pretoria (South Africa) and hence the name zebra battery. The technical name for the battery is Na-$NiCl_2$ battery.

perature operation, zebra batteries allow for the use of latent heat for fast cabin heating or window defrosting. But the thermal management needs for the high-temperature zebra batteries are not ideal for electric vehicle-drive-systems. When not in use, zebra batteries typically require being plugged into wall plug, or tethered, in order to be ready for use when needed. If shut down, a reheating process must be initiated that requires about one to two days to restore the battery pack to the desired temperature, and fully charging the batteries. This reheating time can, however, vary depending on the state-of-charge of the batteries at the time of their shut down, battery-pack temperature, and power availed for reheating. If shut down of the battery pack is desired, three to four days are usually required for a fully-charged battery pack to lose its significant heat. However, this technology has been virtually abandoned by the auto industry due to safety concerns and the catastrophic failures experienced due to freezing.

3.2. Fuel cells

Like storage batteries, fuel cells deliver energy by consuming electroactive chemicals, but differ significantly in that these chemicals are delivered on-demand to the cell. As a result, a fuel cell can generate energy continuously and for as long as the electroactive chemicals are provided to the cell. Typically, these chemicals consist of a hydrogen-rich fuel supplied to the anode and air to the cathode. Although, the first hydrogen-oxygen fuel cell was demonstrated as early as in 1839 by Sir William Grove, the surfeit of rich development in fuel cell technology has come about practically during the last 50 years; initially with developments for the space industry in the sixties, followed by the energy crisis of the seventies, and more recently with the push to electric cars [6: pp. 251–295].

Although several fuel cell concepts have been tested in the laboratory, the systems that are being potentially considered for commercial development are: (i) Phosphoric Acid Fuel Cells (PAFCs), (ii) Alkaline Fuel Cells (AFCs), (iii) Molten Carbonate Fuel Cells (MCFCs), (iv) Solid Oxide Fuel Cells (SOFCs), (v) Polymer Electrolyte Fuel Cells (PEFCs), and (vi) Solid-Polymer-Electrolyte Direct Methanol Fuel Cells (SPE-DMFCs).

3.2.1. Phosphoric acid fuel cells (PAFCs)

Phosphoric acid fuel cells for terrestrial applications have shown promise for commercialization. PAFCs operate at ~200°C with ion conduction through electrolyte being provided by protons.

Platinum and platinum-metal alloys are employed in PAFCs as electrocatalysts with carbon-based electrodes. At such high temperatures, the problems of the stability of the carbons as also the catalysts arise. The advantages of PAFCs are that the phosphoric acid is very stable and can be highly concentrated (~100%) such that the water vapor pressure is low and hence keeping the steady-state water removal by the reactant gases equals the product water rate. Besides, at 200°C, the anode performance is good even with fuels containing carbon-mono-oxide up to 5%. But, PAFCs suffer from slow kinetics for oxygen reduction reaction due to the strong adsorption effects of anions on to the active sites of the catalyst.

3.2.2. Alkaline fuel cells (AFCs)

Alkaline fuel cells are the most promising systems for space applications and have been used successfully in Apollo and other space missions. The advantages of AFCs are that they operate at room temperature, the cathode performance is much superior, and the construction materials are less costly than PAFCs. But, the alkaline electrolytes react with carbon dioxide to form carbonates, which severely limits the cell performance necessitating its scrubbing in the system. Owing to this drawback, presently AFCs are not being considered for terrestrial applications.

3.2.3. Molten carbonate fuel cells (MCFCs)

Molten carbonate fuel cells have several advantages over PAFCs. They have higher power density and higher cell voltages than PAFCs. The electrolyte employed is generally a mixture of alkali metal carbonates and the ion conduction is through the carbonate ions. These salts function as electrolyte only in liquid phase, and therefore the cell operates at 600–700°C. Since the cell is tolerant to carbon-mono-oxide, reforming processes can occur within the fuel cell, and hence reformers and shift converters are not required. Higher efficiencies are achieved since the reforming process absorbs heat, which is supplied in situ by the heat produced at the electrodes of the cell. However, at high temperatures several constraints arise on materials suitability for long-time operations. Furthermore, MCFCs present a more difficult problem in carbon dioxide removal than AFCs because about four times more carbon dioxide per kW of power output has to be transferred in a MCFC plant in relation to an AFC plant.

3.2.4. Solid oxide fuel cells (SOFCs)

Solid oxide fuel cells employ solid, non-porous metal-oxide based electrolytes with ion conduction occurring through the migration of oxide-ions in the crystal lattice. Stabilized zirconia is commonly used as the electrolyte and the operating temperatures of the cells are between 900–1100°C. In recent years, the discovery of the strontium- and magnesium-substituted lanthanum gallate perovskite and $Ce_{0.8}Gd_{0.2}O_{1.9}$ electrolytes that have appreciable oxide-ion conductivity at ~600°C has provided the possibility of developing intermediate-temperature SOFCs operating between 600–700°C. SOFCs have distinct advantages over aqueous electrolyte fuel cells as these employ no liquids and hence the problems associated with the flooding of porous electrodes and the maintenance of 3-phase interface are totally averted. Also, the electrolyte remains invariant and is independent of the compositions of the fuel and oxidant. Since the cell operates at high temperatures, losses due to activation polarization are minimized which avoids the use of noble metal catalysts. In addition, these fuel cells do not suffer from the constraints associated with MCFCs, which require recycling of carbon di-oxide at the cathode.

3.2.5. Polymer-electrolyte fuel cells (PEFCs)

Polymer-electrolyte fuel cells employ an ion-exchange membrane, for example, Nafion®—a hydrated perfluoro sulfonic acid, as electrolyte, which is impermeable to gases. PEFCs hold certain advantages over those with immobilized electrolytes

as they provide a non-volatile electrolyte below 100°C, a drastic reduction in corrosion, and materials related problems, negligible electrolyte leaching (as water is the only reaction product), and a thin electrolyte layer. Polymer electrolytes have excellent oxygen solubility and diffusivity characteristics and are therefore expected to yield better performance than any of the fuel cell systems discussed above. The main disadvantage is the necessity to humidify the electrolyte during its operation.

3.2.6. Solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs)

SPE-DMFCs employ methanol directly as the fuel and hence eliminate the complexity of the reformer unit in the system. Since the methanol is fed with ample water, it also avoids complex humidification and thermal management problems associated with the PEFCs. Consequently, SPE-DMFCs provide the advantage of lower system size as well as weight in relation to any of the existing fuel cell systems. But, SPE-DMFCs suffer from methanol cross-over problem across the Nafion membrane which affects the performance of the cathode and hence the cell during its operation.

It is noteworthy that among the fuel cell systems discussed above, only PEFCs, AFCs and SPE-DMFCs are considered fit for electric cars (Table 2). At present, however, only PEFCs and SPE-DMFCs are being considered as serious contenders since, as indicated earlier, AFCs require pure CO_2-free hydrogen and oxygen (or air) to avoid carbonation of the electrolyte. As is seen from Table 2, SPE-DMFCs can provide a comparable efficiency in relation to PEFCs.

3.3. Electrochemical supercapacitors

Electrochemical supercapacitors (ECs), also called ultracapacitors, are unique devices exihibiting 20–200 times larger capacitance than a conventional capacitor which consists of two plates separated by a gas or vacuum as the dielectric. The large capacitance values exhibited by ECs arise from the combination of the double-

Table 2
Efficiencies and envisaged applications of various fuel cell systems

	PAFC	PEFC	MCFC	SOFC	AFC	DMFC
Electrical system efficiency (%)	36–45	32–40	43–55	43–55	26–31	~40
Some applications[a] cogeneration	2*	1*	3*	4*		
Utility power	3*		2*	1*		
Distributed power	3*	4*	2*	1*		
Utility repowering	3*		2*	1*		
Passenger vehicles		3*			1*	2*
Heavy duty vehicles	2*	4*		1*		3*
Portable power		2*				1*
Speciality power		3*			1*	2*

[a] The degree of priority increases with number of asterisks.

layer capacitance and a pseudocapacitance associated with the participation of adsorbed intermediates in a surface redox reaction.

When an electronic conductor is brought into contact with an ionic conductor, a charge separation takes place on either side of the interface leading to the development of an electrical double-layer. No charge-transfer takes place across the interface and the current observed during this process is essentially non-faradaic in nature. By contrast, there is a faradaic exchange of charge associated with redox reaction which is stored in the form of adsorbed species that can be restored by reversing the process.

In recent years, phenomenal progress has been made in the development of ECs [7]. At present, the development of non-aqueous systems appears to be gaining momentum due to the increased energy density of such systems. Gel electrolytes hold the promise of combining the advantage of solid-polymer electrolytes with the increased voltage of non-aqueous systems. Nevertheless, only the carbon and the RuO_x systems have so far been commercialized while other systems are under various stages of development.

ECs have a number of advantages over storage batteries. ECs can be both rapidly charged and discharged, and can deliver power densities in excess of 1 kW/kg albeit at relatively low energy densities, typically less than 10 Wh/kg. ECs can be configured both in unipolar and bipolar configurations, require little maintenance, and are made from non-toxic and relatively inexpensive materials. With these characteristics, ECs appear ideally suited for meeting the burst acceleration power requirements of an electric car at relatively low-weight penalty.

4. Assessment of electrochemical power sources for electric cars

With the above background of storage batteries, fuel cells and supercapacitors, we will now picture the perspective of these options for electric cars. The power and energy density parameters of the storage batteries discussed in Section 3.1 are given in Table 3. From the cost perspective, lead-acid batteries appear to be the most

Table 3
A comparison of the most promising storage batteries for electric cars

Cell type	Nominal voltage (V)	Specific energy (Wh/kg)	Energy density (Wh/l)	Specific power (W/kg)	Power density (W/l)	Self discharge (%/month)	Cycle life
Lead-acid	2.0	35	70	~200	~400	4–8	250–500
Lithium-ion	3.6	115	260	20–250	400–500	5–10	500–1000
Lithium-Polymer	3.0	100–200	150–350	>200	>350	~1	200–1000
Nickel-Cadmium	1.2	40–60	60–100	140–220	220–350	10–20	300–700
Nickel-metalhydride	1.2	60	220	130	475	30	300–500
Zinc-air	1.2	146	204	150	190	~5	~200
Zebra	2.6	100	160	150	250	~1	~1000

attractive, but with an energy density of only about 35 Wh/kg, almost 6 kg of battery is required to drive a car for 1 km. Coupled with its relatively slow recharge characteristics, it is immediately apparent that the lead-acid battery, in spite of its technical maturity and low-cost, is an unacceptable option. Indeed, the failure of General Motor EV1 to find consumer acceptance may, at least in part, be linked to its dependence on lead-acid batteries [2]. When the high-temperature zebra batteries are rejected for their inability to offer acceptable intermittent operational performance, it is seen from Table 3 that the most viable battery systems are either the nickel-metal hydride or lithium secondary types. Even neglecting the high cost of these battery systems, their energy densities still require 2–2.5 kg of battery to travel 1 km. At 1 kg/km, the zinc-air battery is approaching an acceptable performance, but technical difficulties in achieving a truly rechargeable system continue to frustrate their commercial implementation. It is noteworthy that the vanadium redox and zinc-bromine flow batteries have also been projected as possible contenders for vehicular traction. These batteries, however, have problems of excessive self-discharge. Besides, vanadium and bromine are highly toxic.

The relative power and energy densities of the current generation supercapacitors, storage batteries and fuel cells may be summarized in a Ragone diagram of the type shown in Fig. 2. As discussed earlier in Section 2, the overall energy demand of a modern electric car is about 200 Wh/km, in which case the power plant should be capable of delivering in excess of 500 Wh/kg for it to be within acceptable limits

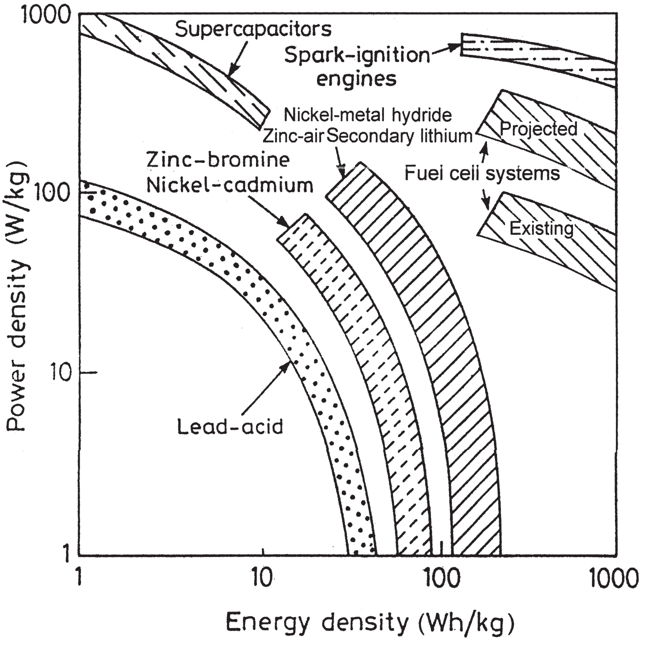


Fig. 2. A Ragone plot comparison of power and energy densities for existing supercapacitors, storage batteries, fuel cells (including reformer), and spark-ignition engines.

in relation to the energy-density range of the spark-ignition engines. It is immediately apparent that this cannot be achieved by any of the direct electric energy storage systems, namely supercapacitors or batteries, and that it is unlikely to be an achievable target for these systems within the foreseeable future. At best, storage batteries and supercapacitor powered vehicles may be able to find limited niche applications in short-range commuter vehicles, especially where the relatively long recharge times can be accommodated by the pattern of vehicle usage.

For transportation, the low-operating temperature and rapid start-up characteristics, together with its robust solid-state construction give the polymer-electrolyte fuel cell (PEFC) a clear advantage for application in cars. Its energy conversion efficiency is much higher than both the Otto and Diesel versions of the internal-combustion engines. The preferred fuel for the PEFCs is hydrogen. While many strategies for providing hydrogen to PEFCs are presently being evaluated (Fig. 3), the most acceptable proposal appears to be to generate hydrogen on-board and on-demand from liquid hydrocarbons or methanol. The technical challenge, however, lies in modifying large-scale industrial processes like steam reforming or partial-oxidation (POX) reactors to lightweight units that can fit inside the car.

The prototype fuel cell car (NECAR-3) demonstrated by DaimlerChrysler is based on steam reforming of methanol which is relatively easy to process on-board and may be conveniently distributed through the existing service-station infra-structure. Meanwhile, POX reactors for processing gasoline, which is favored by the Department of Energy (DOE) in the US, are being developed by Epyx Corporation. POX offers compact reactors, fast start-up and rapid dynamic response while steam

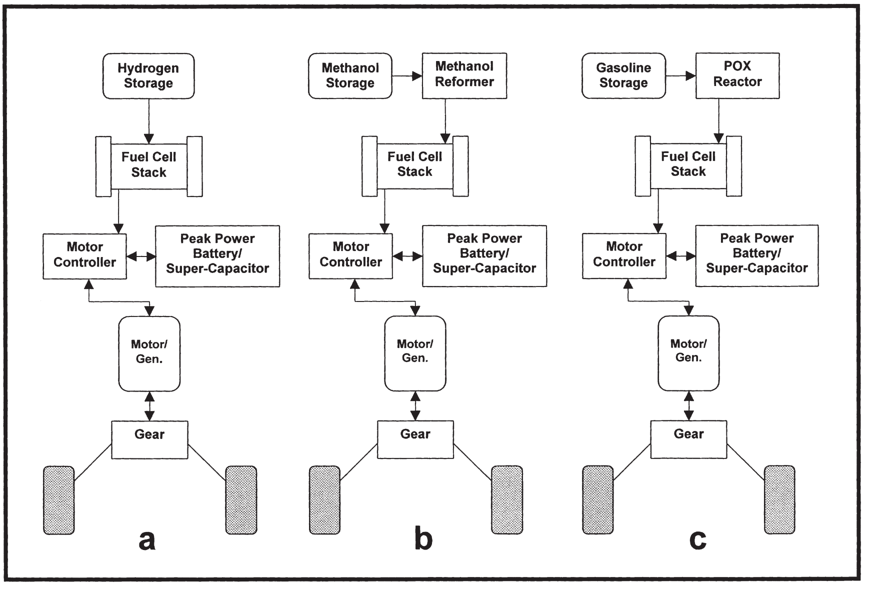


Fig. 3. Feasible fuel cell system configurations: (a) with direct hydrogen fuel, (b) with methanol reformer, and (c) with a partial oxidation (POX) reactor.

reforming produces more hydrogen with an increased efficiency. Johnson–Matthey in the UK have developed a methanol processor called the HotSpot which uses the heat produced by the POX process to drive the steam reforming reaction. This compact system ensures fast start-up and optimum fuel efficiency. But the hydrogen produced by steam reforming and POX of methanol contains carbon dioxide (~20%) and traces of carbon monoxide (~2%). At the operating temperatures of the PEFCs, carbon monoxide even at 0.01% is sufficient to poison the platinum catalyst at the anode. Two strategies to circumvent this problem are under way. Either, carbon monoxide must be removed from the hydrogen stream in a separate process or new carbon-mono-oxide tolerant catalysts need to be developed for deployment at the anode. Production of relatively pure hydrogen from a wide range of commercially available fuels is unarguably the ultimate step in the commercialization of polymer-electrolyte fuel cell cars. North-West Power Systems have recently achieved a milestone in this direction by demonstrating up to 50 liter per minute of pure hydrogen from a methanol fuel processor, as also a successful demonstration of pure hydrogen production using propane and ethanol; with modification, the fuel processor can operate on gaseous feedstock such as methane (natural gas). This multi-fuel processor combines three functions comprising catalytic steam-reforming, heat generation by low-pressure combination of a fuel gas, and hydrogen generation.

An elegant solution to the problems associated with the need for gaseous hydrogen fuel, lies in operating the PEFCs directly with a liquid fuel. Much consideration is therefore being given to PEFCs that run on air plus a mixture of methanol and water. The main technological challenges here are to develop better anode catalysts to overcome efficiency losses at the anode and to improve the membrane electrolyte, and also to find cathode catalysts to prevent its methanol poisoning. A solid-polymer-electrolyte direct methanol fuel cell (SPE-DMFC) would be about as efficient as a conventional methanol reformer/PEFC system. But, since the SPE-DMFCs do not involve any auxiliary units, the development of a commercially feasible SPE-DMFC would be simpler than a PEFC unit, in both its construction and operation. Indeed, SPE-DMFCs are widely regarded as the “holy grail” of fuel cell technologies. The operational difference between a PEFC and a SPE-DMFC electric car is shown in Fig. 4. Ironically, for the present, oil companies the world over are favoring hydrogen from gasoline as the fuel for the future fuel-cell cars, and the political will to project methanol as a fuel is wanting. However, geographically, petroleum is not widely distributed, rendering countries with the largest reserves disproportionate economic and political sway.

At present, the PEFC is emerging as the most viable electric option for the cars. Since the energy density of the PEFC power plant is akin to that of the present-day spark-ignition engines (Fig. 2), comparable driving ranges may be expected. But, the power density of present PEFC systems tends to be lesser than that of the spark-ignition engines. Although, the 80 kW of power needed to provide the acceleration could be supplied by an appropriately-sized PEFC alone, this will probably make the first generation systems excessively large and heavy. Additionally, the high cost of newly developed fuel cells will persuade the car makers to use the smallest cells that will provide the required base power needs of about 50 kW.

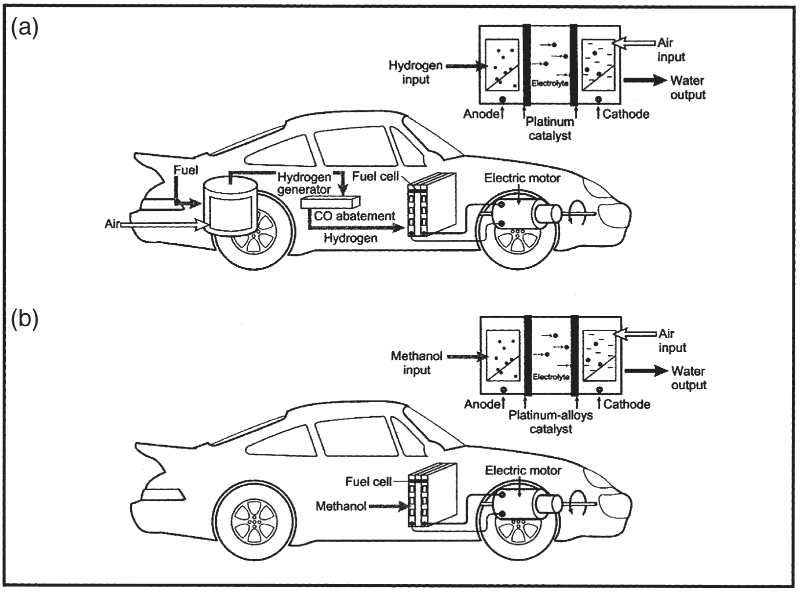


Fig. 4. Operational differences between: (a) a fuel cell electric car with on-board reformer for hydrogen generation, and (b) a fuel cell electric car with direct methanol feed.

An acceptable compromise could be achieved with a supplementary parallel electric storage system using either high power-density supercapacitors or, less likely, storage batteries to provide the short-duration acceleration. This electric storage system could also be used to regeneratively recover the energy, which would be otherwise lost during braking. Since energy density is less important than power density for the acceleration of a car, supercapacitors would appear to be a superior alternative to any of the present storage battery options. But with the development of electric propulsion systems still in its infancy, the final mixing and matching of the electric power options will depend as much on new and refined technological developments as it will on consumer demands. It is however projected to increase the power densities of the PEFC systems to about 300 W/kg by 2004, and significant progress is already being made towards this goal [8]. Such an achievement will help in cutting down both the size and weight of the PEFC systems quite appreciably, and, in future, the entire power requirement of the car could be met with a compact fuel cell system itself. But, even then, the future cars would preferably keep an appropriately sized battery or supercapacitor unit to regeneratively recover the energy during braking which could be used on demand.

In a clear demonstration of its commitment to have fuel-cell cars in series production by 2004, DaimlerChrysler recently unveiled its NECAR-4 version. Its fuel cell power output has been increased by 40%, giving it a top speed of 145 km/h, acceleration to 48 km/h in 6 s, and a range of up to 450 km, which is comparable to conventional ICEVs. Like its predecessor NECAR-3, the new car is based on a Mercedes-Benz A-Class sub-compact car, which has a sandwich floor construction

within which the system can be installed. For the first time, the complete PEFC system is mounted in the vehicle floor, allowing room for up to five passengers and cargo space. It is powered by liquid hydrogen stored in a cryogenic cylinder that takes up a part of the trunk. The engine was developed by Daimler Benz-Ballard (dbb) Fuel Cell Engines GmbH, while the vehicle uses an electric drive train from Ecostar Electric Drive Systems, a joint venture between Daimler Chrysler, Ford and Ballard, which supplied the fuel cell stacks. There was some surprise at the choice of hydrogen as fuel in place of methanol, which powered NECAR-3. But DaimlerChrysler is already working on an advanced fuel cell system which will use methanol as the fuel. According to DaimlerChrysler, for the near term, methanol is not only the clear choice to introduce fuel cell vehicles for consumer use in 2004, but it has long-term environmental benefits because methanol could be produced renewably. DaimlerChrysler believes that the most challenging problems have been solved; the new race is to make them affordable. This is because to achieve widespread acceptance in coming years, the electric cars must have a clear economic advantage over ICEVs.

Today, we stand at the threshold of a new era in alternative vehicular propulsion. Electric vehicles hold the promise of allowing us to continue to enjoy the freedom and mobility that we have become accustomed to and at the same time to do so in a much more fuel efficient, environmentally clean, and sustainable manner. Electric transportation is a reality. The question is: how long will it take to bring it out? But, in the pursuit to develop electric cars, electrochemists will have a vital role.

5. Conclusions

Global environmental, economic and political issues are pushing car manufacturers to build electric power systems as an alternative to the current ICEVs. It is demonstrated that a viable electric car could be operated with a 50 kW PEFC system to provide power for cruising and climbing, coupled in parallel with a 30 kW supercapacitor and/or battery bank to supply the additional short-term burst power during acceleration. Recently, a major alliance between Daimler Benz, Ford and Ballard has been formed to realize and commercialize electric cars. They are committed to have fuel cell cars in series production by 2004.

Appendix A

A.1. Estimation of P_{tyres} at vehicle speed (v) of 50 and 100 km/h

At v=50 km/h: $P_{\text{tyres}} = 0.01\times1400\times9.8\times50\times10^3/3600\ W = 1.9$ kW

At v=100 km/h: $P_{\text{tyres}} = 0.01\times1400\times9.8\times100\times10^3/3600\ W = 3.81$ kW

A.2. Estimation of P_{aero} at vehicle speed (v) of 50 and 100 km/h

In these estimates the wind velocity (*w*) has been taken to zero.

At v=50 km/h: $P_{\text{aero}} = 0.5\times1.17\times0.3\times2.2\times(50)^3\times(10^3)^3/(3600)^3\ W = 1.03$ kW
At v=100 km/h: $P_{\text{aero}} = 0.5\times1.17\times0.3\times2.2\times(100)^3\times(10^3)^3/(3600)^3\ W = 8.27$ kW

A.3. Estimation of P_{grade} at 10% gradient and v =80 km/h

$P_{\text{grade}} = 1400\times9.8\times80\times10^3\times0.1/3600\ W = 30.49$ kW

A.4. Estimation of P_{accel} at v =50 and 100 km/h with an acceleration of 5km/h/s

At v =50 km/h: $P_{\text{accel}} = 1400\times5\times50\times(10^3)^2/(3600)^2\ W = 27$ kW
At v =100 km/h: $P_{\text{accel}} = 1400\times5\times100\times(10^3)^2/(3600)^2\ W = 54$ kW

References

[1] Leggett J. A guide to the Kyoto Protocol: a treaty with potentially vital strategic implications for the renewable industry. Renewable and Sustainable Energy Reviews 1998;4(3):345–51.
[2] Electric Vehicles: Technology, Performance and Potential. OECD/IEA Publications, 1993.
[3] Staff Report. Zero-Emission Vehicle Biennial Program Review. California Air Resources Board. July 6, 1998.
[4] Wicks FE, Marchionne D. Development of a model to predict electric vehicle performance over a variety of driving conditions. Proceedings of the 27th Intersociety Energy Conversion Conference 1992;3:151–8.
[5] Rand DAJ, Woods R, Dell RM. Batteries for electric vehicles. Trauton, UK: Research Studies Press and New York: Wiley, 1998.
[6] Kordesch K, Simader G. Fuel cells and their applications. Weinheim, 1996: VCH, 1996.
[7] Conway BE. Electrochemical supercapacitors: scientific fundamentals and technological applications. New York: Kluwer-Plenum Publishers, 1999.
[8] Chalk SG, Miller JF, Wagner FW. Challenges for fuel cells in transport applications. Jounal of Power Sources 2000;86(1-2):40–51.